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Pesticide Transformation Products Research: A Future Perspective

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Abstract

Pesticide research has largely been restricted to the synthesis, effects, and fate of parent molecules. The identification of primary, secondary, and subsequently formed transformation products, and the toxicological evaluation of those products of potential environmental concern are crucial to create a much needed data-base on pesticide transformation products. The establishment of new regulatory policies will largely depend upon scientific information generated in the coming years.

Disciplines

Entomology | Environmental Health | Plant Biology | Plant Sciences | Toxicology

Comments

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Chapter 20

Pesticide Transformation Products Research

A Future Perspective

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Pesticide research has largely been restricted to the synthesis, effects, and fate of parent molecules. The identification of primary, secondary, and subsequently formed transformation products, and the toxicological evaluation of those products of potential environmental concern are crucial to create a much needed data-base on pesticide transformation products. The establishment of new regulatory policies will largely depend upon scientific information generated in the coming years.

Research on synthetic pesticides has been conducted for the past 50 years. Most research efforts, however, have focused on the parent compound per se. Except for studies concerning metabolism or the identification of products, little attention has been paid to the fate and significance of the products formed from pesticide transformation (1-4). The slow progress in the field of pesticide transformation products can be attributed to three factors: [1] low concentrations at which such products are formed in the environment, [2] assumption that pesticides are generally mineralized to insignificant products, and [3] lack of suitable analytical techniques.

Analytical Techniques

Many transformation products are more water soluble than their respective parent compounds. Difficulty in extracting, separating, and analyzing polar transformation products present in the environmental matrices is one of the many constraints on transformation products research. Volatile metabolites also present unique challenges to sample processing and analysis. Because pesticide metabolites are usually present at trace levels, isolating sufficient quantities of metabolites for identification can be a formidable problem. In addition to the extraction difficulties,

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analytical techniques commonly used to detect parent compounds are not always adequate to detect the transformation products. Liquid and gas chromatography, mass spectrometry, and radiotracers are used to qualitatively and quantitatively detect trace levels of degradation products in complex matrices. New technologies that are being employed include supercritical fluid extraction and chromatography, fluorescence, electrochemical and photodiode array detection, immunoassays (radio and enzyme-linked), biosensors, headspace analysis, and solid-phase nuclear magnetic resonance. As even more sensitive, efficient, and economical techniques of analysis are developed, our understanding of the significance of pesticide transformation products will be enhanced.

Radiotracers. Although the first radiolabeled pesticides were synthesized in 1952 (5), the use of radioassays in plant, soil, and animal metabolism studies has become widespread only since the 1970's. Before the use of radiotracers, the environmental fate of most pesticides was not adequately understood, and the concept of bound residues did not exist. The high cost and difficulty involved in synthesis have resulted in few degradation products being available in radiolabeled form. But labeled degradation products of commonly used pesticides such as atrazine and 2,4-D have been instrumental in detailed investigations of these compounds. Because certain pesticide degradation products are of significance in crop protection and environmental contamination, the synthesis of radiolabeled degradation products in addition to that of the parent compound is emerging as a requisite for the development of new pesticides.

Secondary Degradation Products

The degradation of a pesticide is not completed with the formation of primary degradation products. For several pesticides, the primary degradation products are unstable and are converted to secondary and tertiary degradation products. Relatively few studies have investigated the significance of the latter. The enhanced biodegradation of isofenphos is attributed to the nutritional substrate value of its secondary metabolite, salicylic acid, rather than to that of isopropyl salicylate, its primary metabolite, which does not induce enhanced biodegradation of the parent compound (3). Although the enhanced biodegradation of carbofuran has been well documented, the mechanisms involved are not completly understood. It has been suggested that the secondary metabolite, methylamine, is the possible substrate involved in the enhanced biodegradation process (3). Feusulfothion, an organophosphorus insecticide, is hydrolyzed by *Klebsiella pneumoniae* to 4-methylsulfinyl phenol, which is reduced to a secondary metabolite, 4-methylthiophenol. Because of the inhibitory effect on *K. pneumoniae*, this secondary metabolite is not biodegradable (6). Some secondary metabolites, including aldicarb sulfone, have been detected in surface-water and groundwater samples (7).

Interactions

Intensive agriculture requires the use of several agrochemicals (pesticides, fertilizers, growth hormones). In crop protection, herbicides, insecticides, and fungicides are applied to control a wide range of pests. The degradation of these chemicals often results in the formation of many breakdown products. The presence of several degradation products from a number of agrochemicals could result in interactions of these products either among themselves or with the parent compounds. The interactions could result in additive, synergistic, antagonistic, or potentiation effects. The implications of these interactions in crop protection and environmental contamination could have an important bearing on the use of the agrochemicals.

Regulatory Policies

Regulatory policies on transformation products are less than adequate, primarily because of the lack of scientific data supporting the development of new policies. The U.S. Environmental Protection Agency's requirements for the registration and reregistration of pesticides include identification of degradation products formed at levels > 10% of the applied pesticide. A mere identification is not sufficient, and to understand the significance of these products, more environmental fate and toxicological studies are required. In Canada, plans are in the offing to include in the Pest Control Product Act required toxicity tests for degradation products formed at concentrations exceeding 10% of the applied pesticide in laboratory or field studies (8).

An area of major concern with reference to regulatory policies and degradation products is groundwater contamination (9). In recent years, several degradation products have been detected in groundwater (10). The cumulative concentration of the degradation products may be higher than that of the parent compound (11). The environmental behavior and toxicological effects of some degradation products may differ from those of their parent compounds. The current enforcement standards, however, are only for the parent compounds. Because of the lack of toxiciology data, the toxicological effects of atrazine degradation products are assumed to be similar to those of atrazine itself (9). Atrazine is only the first instance, and in the future the same concerns may arise for other pesticides. A greater understanding of the environmental chemistry and environmental toxicology of pesticide degradation products will contribute to the informed regulatory policies of the future. The cost involved in conducting these studies will also be an important factor in deciding the extent to which transformation products will be investigated.

Future Research Needs

Research on the bioactive products of propesticides, on the role of degradation products in influencing the fate of parent compounds, and on phytotoxic and pesticidal potentials will promote understanding of the role of degradation products in crop protection. From the environmental perspective, a vast majority of the pesticides are transformed to products of less toxicological concern. Toxicological studies (including carcinogenicity and mutagenicity potentials) and environmental fate studies (movement and sorption characteristics, persistence in the surface soil and subsoils, and identification and bioavailability of bound residues) need to be conducted for transformation products of potential environmental and/or public health concern. The influence of the interactive effects of degradation products with other chemicals present in the environmental matrices also needs to be elucidated. The scientific information generated will be useful in developing health advisory levels and regulatory policies for transformation products. If this information is generated before the introduction of new pesticides, pesticides possessing transformation products of potential environmental significance could be identified in the early stages of development.

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